Solvent Decomposition in Li-Ion Battery Electrolyte by DFT Calculations

Ken Tasaki

MC Research and Innovation Center
Mountain View, CA 94041

Introduction

Side reactions involving solvent decompositions at electrode-electrolyte interface play a critical role affecting the Li-ion rechargeable battery capacity, cycle life, safety, and others, thus understanding the interfacial side reactions is essential to be able to control the battery overall performance.

It is widely known that with graphite as the anode, a solid-electrode interface (SEI) film can be formed on the surface of graphite in the ethylene carbonate (EC) electrolyte, while when propylene carbonate (PC) is used as the solvent, exfoliation of graphite occurs and no SEI is formed.[1] However, PC can be a practical rechargeable battery electrolyte solvent when an additive such as vinyl carbonate (VC) is added to the electrolyte, thus forming a SEI film.[2] Search for such additives in forming an effective SEI film has not been straightforward and is currently a subject of intense research effort.[2,3]

Li, et al. have studied the two-electron reduction mechanism of EC by ab initio HF/6-31G* calculations.[4] However, no discussion on the effect of an SEI additive was offered. Zhang, et al. have reported the thermodynamic potentials for various solvent reductions, including VC, using DFT calculations.[5] While their calculations reproduced the difference between EC and PC in their SEI film formation, though no quantitative values were provided,[5] their calculations failed to explain the benefit of using VC as an effective additive. Also, the reduction mechanism used in their calculations was based on the one-electron transfer mechanism.

Aubach, et al. proposed the two-electron reduction mechanism based on the component analysis of SEI films as follows:[6]
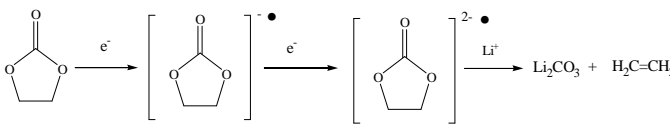
$$(1)$$

We've recently performed DFT calculations for reduction decomposition of various solvents, including VC, based on the two-electron mechanism and report the finding here.

Calculations

The solvents and the additive studied in the calculations included EC, PC, dimethyl carbonate (DMC), diethyl carbonate (DEC), and VC. The first electron reduction energy ($E_1 = E_{11} + E_{12}$) and the second electron reduction energy (E_2) for these compounds were calculated at the B3LYP/ 6-31+G(d,p) level in the following reduction schemes using EC as an example:
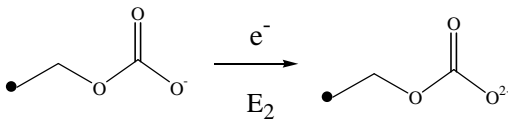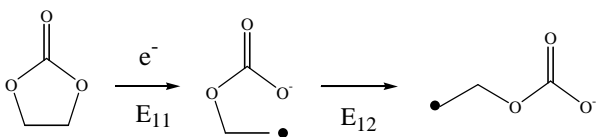
The solution effect was included in the calculations through Tomasi's Polarized Continuuem Model.[7]

Results and Discussions

Table 1 lists the first electron reduction energies (E_1).

Table 1. The calculated values of E_1 (eV)

EC	PC	DMC	DEC	VC
-2.97	-2.95	-1.421	-2.60	-2.54

The order in the likelihood of solvent reduction is EC ~ PC > DEC > VC > DMC, which is similar to the order presented by Zhang, et al.[5] Thus, if one were to look only at the values of E_1 (one-electron reduction), no insight would be obtained for the favorable effect of VC as an additive for SEI film formation. Table 2 lists the second electron reduction energies (E_2).

Table 2. The calculated values of E_2 (eV)

EC	PC	DMC	DEC	VC
-2.85	-2.58	–	–	-3.82

Now, the order becomes VC > EC > PC in the likelihood of the second electron transfer reduction. Here, VC has the lowest value of E_2 among the solvents studied and is likely to undergo the second-electron reduction to produce Li_2CO_3 which is found in most of SEI films, according to eq (1). On the other hand, PC alone, having a relatively high value of E_2, may be decomposed before undergoing the second-electron reduction. Thus, our results are consistent with the effectiveness of VC as an SEI film additive. The difference between EC and PC also becomes more apparent, compared to Table 1, relating to the well-known difference in forming an SEI film. The calculations for both DMC and DEC didn't converge, implying their instability in this process. Aubach, et al. found no SEI film formation when DEC was used as a solvent.[6] Our results suggest that the two-electron reduction mechanism be taken into account in understanding the SEI film formation. The effects of Li ion coordination and the salt concentration on solvent decomposition will be also discussed.

References

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